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(12) Patent:

(11) CA 280272

(54) SHALE PROCESSING

(54) TRAITEMENT DU SCHISTE

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ABSTRACT:

CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

(72) Inventors (Country): **WILLIAM HUNTLEY HAMPTON** (Not Available)(73) Owners (Country): **WILLIAM HUNTLEY HAMPTON** (Not Available)

(71) Applicants (Country):

(74) Agent:

(45) Issued: **May 22, 1928**

(22) Filed:

(41) Open to Public Inspection:

(52) Canadian Class (CPC): **196/27**(51) International Class (IPC): **N/A**Patent Cooperation Treaty (PCT): **No**(30) Application priority data: **None**Availability of licence: **N/A**

Language of filing:

Unknown

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WHAT I CLAIM IS:

1. In the treatment of solid bitumeniferous mineral matter to obtain valuable products therefrom, the process which comprises heating such bitumeniferous matter in intimate fluid commixture with an ammonia-liberating base and an oil at temperatures not substantially exceeding about 700°F, and recovering volatilized products.

2. In the treatment of solid bitumeniferous mineral matter to obtain valuable products therefrom, the process which comprises digesting, at temperatures not substantially exceeding about 700°F, such bitumeniferous matter in finely divided condition and in intimate fluid commixture with finely divided caustic lime and a mineral oil, and recovering volatilized products.

3. In the treatment of solid bitumeniferous mineral matter to obtain valuable products therefrom, the process which comprises heating such bitumeniferous matter in intimate fluid commixture with an ammonia-liberating base and an oil at temperatures not substantially exceeding about 700°F, the mixture being agitated and maintained fluid throughout the digestion, recovering volatilized products during digestion, separating residual solid matter from the still fluid mixture after digestion, and distilling such separated solid matter to coke with recovery of distillate.

4. The process as defined in claim 3 further characterized by conducting the cooking distillation at temperatures from about 700°F up to about 900°F.

5. The process as defined in claim 3 further characterized by subjecting the resultant coke, without cooling, to controlled combustion, and recovering ammonia from the combustion gases.

6. The process of treating solid bitumeniferous mineral matter to obtain valuable products therefrom, which comprises digesting an intimate commixture of such bitumeniferous matter and a base, both in finely divided condition, in a mineral oil bath, at temperatures above 500°F, and recovering volatilized products.

7. The process of treating solid bitumeniferous mineral matter to obtain valuable products therefrom, which comprises digesting an intimate fluid commixture of finely divided bitumeniferous matter and a finely divided base with a heavy oil, at temperatures within the approximate range of from 600° to 700°F, to liberate ammonia and volatilize certain hydrocarbon oil fractions.

8. The process of treating solid bitumeniferous mineral matter to obtain valuable products therefrom, which comprises digesting a finely ground mixture of such bitumeniferous matter and not to exceed about 5 per cent of its weight of caustic lime with a heavy mineral oil at temperatures approximating 680° to 700°F, to liberate ammonia and volatilize certain hydrocarbon oil fractions.

9. The process of treating solid bitumeniferous matter, such as shale and the like, to obtain valuable products therefrom, which comprises digesting an intimate mixture of such bitumeniferous matter and a base with an oil at temperatures sufficiently high to liberate ammonia but insufficiently high to cause substantial deposition of carbon, and also recovering valuable hydrocarbons from said mixture.

10. The process of treating solid bitumeniferous matter, such as shale and the like, to obtain valuable products therefrom, which comprises finely grinding together such bitumeniferous matter and lime, digesting the ground material at temperatures within the approximate range of from 600° to 700°F with sufficient heavy mineral oil to provide a fluid digestion mixture, and recovering both liberated ammonia and volatilised hydrocarbons.

11. The process of treating bituminous shale or the like to obtain valuable products therefrom, which comprises preparing a mixture of pulverised shale or the like with caustic lime and enough heavy mineral oil to give the mixture a fluid consistency, digesting said mixture with the aid of agitation at temperatures sufficiently high to liquefy a substantial portion of the shale bitumens but insufficiently high to cause substantial carbon deposition, said mixture remaining fluid during the digestion, recovering ammonia liberated and hydrocarbons volatilised during digestion, separating residual solid matter from the digestion mixture, and destructively distilling such separated solid matter.

12. The process of treating bituminous shale or the like which comprises heating and agitating a fluid mixture of finely ground shale, finely ground caustic lime and a heavy mineral oil, at temperatures above 500°F but not substantially exceeding 700°F, and recovering liberated ammonia and volatilised hydrocarbons.

13. The process as defined in claim 12 in which approximately 1 to 2 per cent of lime is employed in the mixture.

14. The process as defined in claim 12 characterized by the further steps of destructively distilling the residual solid matter from the digestion to obtain coke and further volatile matter including ammonia.

15. The process as defined in claim 9, further characterized by the fact that the digestion is carried on at temperatures approximating 680° to 700° F.

16. The process as defined in claim 11, further characterized by the fact that the digestion is carried on at temperatures approximating 680° to 700° F.

17. In the art of obtaining valuable products from solid bitumeniferous mineral matter, the process which comprises destructively distilling to coky condition an intimate commixture of such mineral matter and lime at temperatures not substantially exceeding 900° F., and recovering a resultant distillate. C

18. The process of treating solid bitumeniferous mineral matter which comprises digesting such matter in finely divided condition at temperatures above 500° F. in admixture with mineral oil and a reagent capable of binding sulfur present in reactive state under the conditions of operation, and collecting a distillate.

19. The process of treating bituminous shale or the like which comprises digesting, at temperatures above 500° F. but not substantially higher than 700° F., a fluid mixture comprising finely divided shale, a heavy mineral oil, and a relatively small proportion of caustic lime, and collecting distillate from the digestion.

Signed at Portland, Oregon, this 16th day of
July, 1923.

Wm. Huntley Hampton

In the presence of:

G. C. Lyman

V. Victoria Hampton

This invention relates to Art of Treating Shale and Other Bitumeniferous Solids; and in particular the invention has to do with the digestion of shale or the like with a heavy mineral oil, in intimate mixture with a relatively small proportion of an added ammonia-liberating base, such as caustic lime, under conditions of temperature such that complex nitrogen compounds present in the bitumeniferous mineral are decomposed at least to a substantial extent with liberation of ammonia which can be recovered by suitable means concomitantly with recovery of valuable hydrocarbon oil fractions vaporized during the digestion process, while at the same time sulfur present in reactive condition is bound or fixed and its evolution as hydrogen sulfid and analogous undesirable volatile sulfur compounds is substantially suppressed.

In prior copending applications I have disclosed and claimed methods of treating shale and other bitumeniferous solids by digesting the same in finely divided condition and in fluid admixture with a relatively heavy mineral oil at temperatures preferably ranging from about 600° to 700°F, and recovering hydrocarbon oil fractions vaporized during the digestion, the residual solid mineral matter remaining after the digestion being then most desirably separated from the accompanying unvaporized oil and bitumens and subjected to destructive distillation for recovery of hydrocarbon products from such bitumeniferous matter as may have resisted the liquefying and resolving action of the digestion oil. The process thus briefly outlined has proved thoroughly success-

ful but in carrying the same out in practice I have now found it especially advantageous to introduce certain modifications that achieve and increase the efficiency and economy of the process and otherwise favorably affect the results attained. The bitumens present in oil shale and like mineral matter practically always contain appreciable percentages of nitrogen in complex combination. Sulfur may also be present either in organic or inorganic combination, or both. The nitrogen exists partly in combination with hydrogen and carbon, and sometimes also with sulfur, in the form of amide or amide-sulfur compounds.

Under the conditions of digesting shale with oil in accordance with the procedures disclosed in my prior applications aforesaid, practically none of the nitrogen existing in these complex forms is liberated as ammonia during digestion. The oil fractions vaporized during digestion and recovered as condensates, as well as the residual unvaporized body of oil comprised in the digested mixture, contain nitrogen compounds; and so does the residual solid bituminous matter that has resisted or escaped the breaking-down action of the hot oil bath. The nitrogen compounds present in the various oil fractions cause the oils to darken upon standing and to deposit resinous asphaltic substances insoluble in oils but soluble in certain solvents such as alcohol or benzol. The aforesaid residual solid bituminous matter, upon separation from the digestion mixture and destructive distillation, yields ammonia in free or available form due to pyrogenic decomposition of the bituminous content.

The sulfur content of the original shale or other bitumeniferous mineral treated may be present as a constituent

of or associated with bitumen complexes, in which form it is highly detrimental because it is largely reactive at the digestion temperatures in question and is evolved as hydrogen sulfid or analogous volatile sulfur compounds when digested at 570° to 700°F under the conditions of operation set forth in my prior applications aforesaid. On the other hand, sulfur present in the form of iron pyrites, which are carried by some shales, is not evolved during digestion, iron pyrites being substantially inert at the temperatures of digestion. Similarly stable compounds such as sulfates are not affected.

It is therefore a principal object of the present invention to so conduct the digestion treatment of the shale or other bituminous mineral as largely to break down the nitrogen complexes present and to liberate ammonia which can be recovered as a valuable by-product separately from the oil fractions vaporized during digestion, at the same time avoiding formation and deposition of resinous substances of the character above mentioned not only in the lighter oil fractions but also in those not vaporized during digestion. A further object is to bind or fix reactive sulfur in such manner as to suppress its liberation as hydrogen sulfid or in other volatile form while at the same time purifying the hydrocarbon oils produced by the process.

Other objects and advantages of the invention will become apparent as the description proceeds.

I have found that the objects of the invention are attained by carrying out the digestion treatment in the presence of a suitable proportion of a base that will react under the conditions of digestion to liberate nitrogen as ammonia either wholly or to a substantial extent, from the combina-

tions in which it occurs in the mineral; and that will also react to bind reactive sulfur present. Any base capable of reacting to attain these results, can be utilized within the broad scope of the present invention; but for practical purposes it is found advantageous to employ lime as the basic reagent in question, and especially to employ caustic lime (CaO), the hydrated form being usually much less effective. The exact quantity of lime or other basic reagent to be employed in a given instance naturally depends upon the proportions of nitrogen and sulfur contained in the shale in a form which they will react with such base. With the average shale, an addition of 1 to 2 per cent by weight of caustic lime is ordinarily sufficient to accomplish the purposes in view; and it is a very exceptional shale that requires as much as 6 per cent to achieve the results sought.

In order to secure the best results in carrying out the invention, it is of great importance to ensure that the caustic lime or other basic reagent is brought into proper reacting relation with the shale. For maximum effectiveness, both the shale and the lime should be finely pulverized and very intimately commingled. This is best accomplished by grinding the lime and shale together, the shale having been previously dried if necessary so that the lime undergoes little or no hydration during the mixing or blending operation. In a particularly desirable way of accomplishing this grinding in practice, the shale which has been previously coarsely comminuted by rough crushing, together with the necessary amount of added caustic lime and a part or all of the heavy oil to be used in the digestion mixture, are all mixed together by suitable agitating

or stirring means and the mixture is preheated to say 300° or 400°F, at which temperatures the shale becomes comparatively soft and friable and is thus in particularly favorable condition to undergo fine grinding in suitable grinding machinery, whereas without such preheating it is very much more difficult to pulverize. The mixture thus prepared and preheated as described may be run into a ball mill or other suitable grinding device and the solid constituents of the mixture reduced with comparative ease to a fineness such that substantially all of the solids will pass a 100-mesh sieve, and in practice it is found desirable that the grinding or pulverizing be continued until 60% or more of the solids will pass 200-mesh. This treatment achieves a most intimate commixture of the caustic lime with the bituminous mineral, thereby favoring efficient reaction of the lime upon the decomposable nitrogen compounds of the mineral during the subsequent digestion with liberation of ammonia on the one hand, and binding of reactive sulfur as calcium sulfide (CaS) on the other. Furthermore, fine grinding effectively exposes the refractory bitumens of the shale to the liquefying and decomposing action of the heavy digestion oil.

The oil used for the digestion bath may vary considerably in character but it should desirably consist wholly or in substantial part of oil fractions that do not vaporize extensively at or below 700°F. In starting operations, this oil may be a stripped oil, a grade of steam cylinder stock known commercially as Congo cylinder oil being suitable, for example. After the process has been operating for a sufficient period, the digestion oil used may be the heavier fractions of oil derived from the shale itself. In some cases it is advantageous to employ crude petroleum for making up the digestion bath. The amount

of heavy oil so commingled with the shale and lime may vary considerably depending upon the character of the particular shale to be treated. In the case of a typical Colorado shale that normally yields about 30 gallons of oil per ton by the ordinary Scotch distillation method, mixing about one volume of heavy oil with two volumes of crushed shale gives good results. Richer shales require relatively less heavy oil, and leaner shales more. The quantity of caustic lime used is advantageously somewhat in excess of that theoretically required to effect the desired ammonia liberation and sulfur fixation, especially since the breaking down of some of the oxygenated bitumens during the digestion apparently effects hydration of the lime to some extent and thus reduces its activity at this stage of the process, although this hydration is of advantage at a later stage, as will hereinafter be pointed out. As a rule, the use of two per cent by weight of caustic lime, figured on the weight of the shale, is sufficient, and in many cases one per cent is enough.

The finely ground mixture prepared as above described should be fluid in general character, a slurry-like consistency being suitable. The temperature of digestion should be high enough to bring about the desired liquefaction and breaking down of the shale bitumens in the oil digestion bath. At the same time the temperature should not be allowed to go high enough to cause the far-reaching decomposition of the oil hydrocarbons with deposition of free carbon and formation of coke which characterizes what is commonly termed "cracking". In practice it is found desirable to maintain the digestion bath at above 500°F, a range of from 600° to 700°F being suitable, and the optimum range being about 680° to 700°F. The fluid mass should also be

thoroughly agitated continuously throughout the digestion to cause constant rubbing of the mineral particles upon each other and thus expose fresh surfaces to the hot oil bath. It may be noted here that the action of the hot oil bath on the shale bitumens is not merely a liquefying or solvent action, but involves a chemical breaking down and decomposition of said bitumens into lighter products. The heavy oil added to the shale in making up the digestion mixture is also in its turn broken down to yield lighter products, due apparently to chemical interaction between said oil and the shale bitumens under the conditions of digestion.

During the digestion, ammonia is liberated and comes off with the oil vapors and the steam generated in the reaction, but no sulfuretted hydrogen is evolved the reactive sulfur being bound by the lime. The oil vapors may be fractionally condensed to produce commercial distillates and the ammonia scrubbed out or otherwise recovered according to known methods. The unvaporized portion of the digestion mixture is treated, as by centrifuging, or by dilution with a lighter oil and sedimentation, to separate residual solid matter or "tailings", the oil separated from such tailings being amenable to treatment for production of valuable lubricating oils, for example. The oils, both heavy and light, obtained as described, have much less tendency to darken in color, and remain much clearer than when lime is not added to the mixture. Moreover they do not deposit resinous matter upon standing.

It should be noted that carbonates of lime and magnesia, which are often carried by shales, do not function usefully in the present process and do not

produce the results sought.

The digestion can be carried on in any suitable digester equipped with stirring means and provided with a vapor offtake leading to a condenser system. The stirring means may advantageously serve to advance the fluid digestion mixture in a systematic manner from a point offered to a point of discharge. Apparatus of this general type being known in the art, no detailed description thereof is necessary here.

The residual solids or tailings from the digestion having been washed with a light oil and dried, may be destructively distilled to obtain further hydrocarbon oils from such bituminous matter therein as resisted or escaped the action of the hot oil bath, and also to obtain more ammonia. The character of the tailings is such that this can be effected at temperatures ranging from 700°F initial to 900°F final, the final temperature being obviously much lower than is required in the Scotch process. This is because the prior digestion has rendered the residual bitumens less refractory and more amenable to heat treatment. As regards the ready liberation of ammonia, the partially hydrated lime serves to supply the steam needed at the higher temperatures of destructive distillation to aid in the ammonia-forming reactions. It is to be noted in this connection that as a result of the prior digestion the lime is present in peculiarly intimate commixture with the residual solids and can thus react most effectively. The distillation is carried to cokes, the hydrocarbons and ammonia driven off being recovered by known methods.

The total yield of oils from shale treated by the method hereinabove described is far greater than by the ordinary Scotch destructive distillation of raw shale, and

the ammonia recovery is also larger and is obtained at much lower temperatures.

The invention has been described more particularly with reference to treatment of bituminous shale, for the sake of a concrete example illustrating the broad principles involved and also because the invention at present finds its most important practical application in that field. Moreover, the treatment of shale is a problem distinct from the treatment of other bitumeniferous solids owing to the peculiarly refractory and resistant character of the bitumens contained in shale which has baffled many attempts to extract said bitumens by means of solvents. However, the principles of the invention are also applicable to other bitumeniferous solids such as coals, peat, lignite and the like, which can to advantage be commingled in finely divided condition with lime and a heavy oil, digested as before described, and the tailings destructively distilled to cokes, the process yielding valuable hydrocarbon oil fractions, ammonia and coke by the rational and relatively low-temperature treatment set forth.

In the treatment of shale and peat, where the coky residue from destructive distillation of the tailings is usually of too low calorific value for direct use as fuel, there may be a third stage in the ammonia recovery, as follows: The fixed carbon of the aforesaid coky residue, and whatever carbon compounds have survived the final heating to 900°F., are in highly active condition at the close of the distillation and will take fire readily if exposed to air. By admitting such air into contact with the coky residue in regulated quantity, partial combustion may be effected whereby the temperature is considerably raised and further ammonia liberated and recovered. By proper control of the

air admission, a type of producer gas can also be obtained.